



09/841800

CJC

Attorney Docket No.: PATENT
SSI-02001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of)	Group Art Unit: 2825
Maximilian A. Biberger)	Examiner: Caridad Everhart
Patent No. 6,890,853 B2)	TRANSMITTAL LETTER
Serial No. 09/841,800)	
Issue Date: May 10, 2005)	162 North Wolfe Road
Filed: April 24, 2001)	Sunnyvale, CA 94086
)	(408) 530-9700
For: METHOD FOR DEPOSITING)	
METAL FILM AND METAL)	Customer No. 28960
DEPOSITION CLUSTER TOOL)	
INCLUDING SUPERCRITICAL)	
DRYING/CLEANING MODULE)	

Attn: **Decision and Certificate of Correction**
Branch of the Patent Issue Division

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Attached please find an addendum to request Certificate of Correction including a copy of the printed U.S. Patent No. 6,001,133 for filing with the U.S. Patent and Trademark Office.

The Commissioner is authorized to charge any additional fee or credit any overpayment to our Deposit Account No. 08-1275. **An originally executed duplicate of this transmittal is enclosed for this purpose.**

Respectfully submitted,
HAVERSTOCK & OWENS LLP

Dated: July 14, 2006

By: Thomas B. Haverstock
Thomas B. Haverstock
Reg. No. 32,571

Attorneys for Applicant

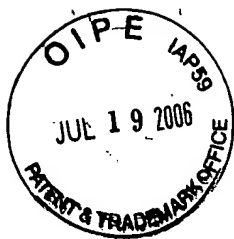
CERTIFICATE OF MAILING (37 CFR § 1.8(a))

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HAVERSTOCK & OWENS LLP

Date: 7/14/06 By: [Signature]

AUG 09 2006



PATENT
Attorney Docket No.: SSI-02001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Biberger et al.

Patent No. 6,890,853 B2
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Issue Date: May 10, 2005
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For: **METHOD OF DEPOSITING
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DEPOSITION CLUSTER TOOL
INCLUDING SUPERCRITICAL
DRYING/CLEANING MODULE**

) Group Art Unit: 2825

) Examiner: Caridad Everhart

) **ADDENDUM TO REQUEST FOR
CERTIFICATE OF CORRECTION**

) 162 North Wolfe Road
) Sunnyvale, CA 94086
) (408) 530-9700) 833-0160

) Customer No.: 28960

**Attn: Decision and Certificate of Correction
Branch of the Patent Issue Division**

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

A letter of June 20, 2006 from Ms. Cecelia B. Newman, Decisions and Certificate of Correction Branch to the Applicants stated "U.S. Patent No. 6,001,133 is not available and is listed as withdrawn in East."

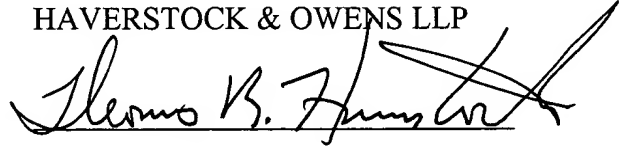
In response, the Applicants wish to make the following points: First, it is not clear from this letter whether the patent was listed as withdrawn in East on February 24, 2004, when it was originally submitted as a reference; second, even though the patent is listed as withdrawn in East, it was published on December 14, 1999, and is available from other sources, such as Westlaw.

ACG 09 2006

For your convenience, a copy of the printed U.S. Patent No. 6,001,133 as originally issued is enclosed so that it can be made of record.

Respectfully submitted
HAVERSTOCK & OWENS LLP

Dated: 7-14-06

By: 

Thomas B. Haverstock

Registration No.: 32,571

Attorneys for Applicant

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HAVERSTOCK & OWENS LLP

Date: 7/14/06 By: 

AUG 09 2006



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United States Patent [19]

DeYoung et al.

[11] Patent Number: 6,001,133

[45] Date of Patent: Dec. 14, 1999

[54] METHODS OF DRY CLEANING WITH COMPOSITIONS WHICH CONTAIN CARBON DIOXIDE AND END FUNCTIONALIZED POLYSILOXANE SURFACTANTS

[75] Inventors: James P. DeYoung; Gina M. Stewart; Bernadette Storey-Laubach, all of Durham, N.C.

[73] Assignee: MiCell Technologies, Inc., Raleigh, N.C.

[21] Appl. No.: 09/143,296

[22] Filed: Aug. 28, 1998

Related U.S. Application Data

[60] Provisional application No. 60/057,063, Aug. 29, 1997, and provisional application No. 60/086,969, May 28, 1998.

[51] Int. Cl.⁵ D06L 1/12

[52] U.S. Cl. 8/142

[58] Field of Search 8/142; 510/291, 510/466

[56] References Cited

U.S. PATENT DOCUMENTS

3,389,160	6/1968	Reid et al.	260/448.2
4,472,566	9/1984	Ziemelis et al.	528/38
4,507,455	3/1985	Tangney et al.	528/26
4,609,750	9/1986	Kollmeier et al.	556/419
4,911,853	3/1990	Coffindaffer et al.	252/8.8
5,026,489	6/1991	Snow et al.	252/8.8
5,087,715	2/1992	Snow	556/413
5,676,705	10/1997	Jureller et al.	8/142
5,683,473	11/1997	Jureller et al.	8/142
5,683,977	11/1997	Jureller et al.	510/286
5,780,553	7/1998	DeSimone et al.	525/276
5,789,505	8/1998	Wilkinson et al.	526/209
5,858,022	1/1999	Romack et al.	8/142
5,866,005	2/1999	DeSimone et al.	210/634

FOREIGN PATENT DOCUMENTS

96/27704	9/1996	WIPO
97/16264	5/1997	WIPO

OTHER PUBLICATIONS

Hoefling et al.; Design and Synthesis of Highly CO₂-Soluble Surfactants and Chelating Agents, *Fluid Phase Equilibria*, 83:203-212 (1993). No month available.
 Matisons et al.; Characterization of Novel Cationic Amino-hydroxysiloxanes, *Macromolecules*, 27:3397-3405 (1994). No month available.

Hoefling et al.; Microemulsions in Near-Critical and Supercritical CO₂, *J. Phys. Chem.*, 95:7127-7129 (1991). No month available.

Hoefling et al.; The Incorporation of a Fluorinated Ether Functionality into a Polymer of Surfactant to Enhance CO₂-Solubility, *The J. of Supercritical Fluids*, 5:237-241 (1992). No month available.

Yazdi et al.; Design, Synthesis, and Evaluation of Novel, Highly CO₂-Soluble Chelating Agents for Removal of Metals, *Ind. Eng. Chem. Res.*, 35: 3644-3652 (1996). No month available.

Newman et al.; Phase Behavior of Fluoroether-Functional Amphiphiles in Supercritical Carbon Dioxide, *The J. of Supercritical Fluids*, 6:205-210 (1993). No month available.

Hoefling et al.; Effect of Structure on the Cloud-Point Curves of Silicone-Based Amphiphiles in Supercritical Carbon Dioxide, *The J. of Supercritical Fluids*, 6:165-171 (1993). No month available.

Xiong et al.; Miscibility, Density and Viscosity of Poly-(Dimethylsiloxane) in Supercritical Carbon Dioxide, *Polymer*, 36(25):4817-4826 (1995). No month available.

Stofesky et al.; The Effect of Hydroxyaluminum Disoaps and Perfluoroalkylpolyethers on the Viscosity of Liquid Propane and Carbon Dioxide, *Proceeding 6th Int'l Symposium on SCFs*, McHugh, M.A., Ed. Johns Hopkins University: Baltimore, MD, pp. 341-344 (1991). No month available.

Saito; Research Activities on Supercritical Fluid Science and Technology in Japan—A Review, *The J. of Supercritical Fluids*, 8:177-204 (1995). No month available.

Yazdi et al.; Design of Highly CO₂-Soluble Chelating Agents for Carbon Dioxide Extraction of Heavy Metals, *J. Mater. Res.*, 10(3):530-5337 (Mar. 1995). No month available.

International Search Report, PCT/US98/17926, Dec. 22, 1998.

Primary Examiner—Caroline D. Liott

Attorney, Agent, or Firm—Myers Bigel Sibley & Sajovec

[57]

ABSTRACT

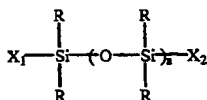
A method for dry-cleaning articles such as fabrics and clothing in carbon dioxide comprises contacting an article to be cleaned with a liquid dry cleaning composition for a time sufficient to clean the fabric. The liquid dry-cleaning composition comprises a mixture of carbon dioxide, water, and an end-functional polysiloxane surfactant. After the contacting step, the article is separated from the liquid dry cleaning composition. The method is preferably carried out at ambient temperature.

4 Claims, No Drawings

Articles that can be cleaned by the method of the present invention are, in general, garments and fabrics (including woven and non-woven) formed from materials such as cotton, wool, silk, leather, rayon, polyester, acetate, fiberglass, furs, etc., formed into items such as clothing, work gloves, rags, leather goods (eg., handbags and brief cases), etc.

"End Functional" Polysiloxane (PSI) materials have specific utility as surfactants in the formulation of CO₂ based cleaning systems. Detergency in non-aqueous cleaning systems is facilitated by surfactants that increase the quantity and stability of entrained water in the system. End Functional PSI materials are differentiated from other functional PSI materials by the locale and orientation of the functional group (e.g., hydrophilic or lipophilic functional groups; preferably hydrophilic functional groups) being at either (or both) termini of the molecules. The term "termini" or "terminus" herein refers to the discontinuation or end of dimethyl siloxane repeat units in the molecule. Thus the functional group is typically covalently joined to a dimethyl silyl group, rather than emanating from a methyl siloxane linkage in the backbone of the polymer.

As noted above, end-functional polysiloxane surfactants used in carrying out the present invention are represented by the formula X₁-A-X₂, wherein X₁ and X₂ are the end-functional groups or moieties (e.g. as described below) and A is polysiloxane group such as polydimethylsiloxane, typically having a molecular weight of 100 or 200 to 100,000, 200,000 or 400,000 g/mole. Such compounds are more particularly represented by the formula:



wherein:

n is from 1 or 2 to 20, 100, 500, 1,000, 5,000, or 10,000. Preferably, n is 1 or 2 to 20, 50 or 100.

At least one, and preferably both, of X₁ and X₂ are CO₂-phobic groups, such as lipophilic or hydrophilic (e.g., anionic, cationic) groups, but are not CO₂-philic groups. The X₁ and X₂ groups may be the same or different. Optionally, but less preferably, one of X₁ or X₂ may be a CO₂-philic group, such as an alkyl or aryl group as the polysiloxane end terminus.

R is alkyl, aryl, or haloalkyl such as perfluoroalkyl. Lower alkyl, particularly methyl, is preferred, trifluoropropyl is preferred, and phenyl is preferred. Methyl is most preferred.

In general, the materials of the invention contain multiple siloxane repeat units that are "CO₂-philic", and CO₂-phobic end-functional groups capable of forming non-covalent associations or positive interactions with desired compounds, such as water, hydrophilic soils, oils, hydrophobic soils, etc.

PSI reactive materials that can be used as precursors for end functional PSI surfactants are silicones with reactive groups that upon reaction with a given substrate yield end functional materials. Reactive groups include but are not limited to; Vinyl, hydride, silanol, alkoxy/polymeric alkoxide, amine, epoxy, carbinol, methacrylate/acrylate, mercapto, acetoxyl/chlorine/dimethylamine moieties.

Additional examples of functional end groups include, but are not limited to, hydrophilic end groups such as ethylene glycol, polyethylene glycol, alcohols, alkanolamides, alkanolamines, alkylaryl sulfonates, alkylaryl sulfonic acids, alkylaryl phosphates, alkylphenol ethoxylates, betaines, quaternary amines, sulfates, carbonates, carbonic acids, secondary amines, tertiary amines, aliphatic amines, polyamines, acetylacetate, carbohydrates, anhydrides, malonic esters, alkyl phosphates, glycidyl ethers, and amino acids (including derivatives thereof), etc.; and lipophilic end groups such as linear, branched, and cyclic alkanes, mono and polycyclic aromatic compounds, alkyl substituted aromatic compounds, polypropylene glycol, polypropylene aliphatic and aromatic ethers, fatty acid esters, lanolin, lecithin, lignins (including lignin derivatives), alkyl sulfates, anhydrides, glycidyl ethers, aliphatic amines, and amino acids (including derivatives thereof), etc.

An example of an end functional PSI material useful in improving the quantity and stability of water in carbon dioxide and also useful in facilitating detergency is 3-[(2-hydroxy-3-diethylamino)propoxy] propyl terminated polydimethylsiloxane. The material has a number average molecular weight of about 200 TO 50,000 g/mole, preferably about 1200 g/mole.

The surfactants of the invention can be employed with any carbon-dioxide dry cleaning system, such as described in U.S. Pat. No. 5,683,473 to Jureller et al; U.S. Pat. No. 5,683,977 to Jureller et al; U.S. Pat. No. 5,676,705 to Jureller et al; and U.S. Pat. No. 4,012,194 to Maffei, the disclosures of which applicants specifically intend to be incorporated herein by reference. Where these prior systems include a surfactant, the surfactants of the invention may be substituted for, or used in combination with, the surfactants described therein.

In one particular embodiment, Liquid compositions useful for carrying out the present invention typically comprise:

- (a) from zero or 0.1 to 10 percent (and when included, more preferably from 0.1 to 4 percent) water;
- (b) carbon dioxide (to balance; typically at least 30 percent);
- (c) surfactant (preferably from 0.001, 0.01, 0.1 or 0.5 percent to 5, 10 or 30 percent); and
- (d) from zero or 0.1 to 50 percent (and in one embodiment from 2 or 4 to 30 percent) of an organic co-solvent.

Where a CO₂-phobic substance is included in the composition, it is typically included in an amount of from 0.01, 0.1, or 0.5 to 10, 30, or 50 percent by weight.

Percentages herein are expressed as percentages by weight unless otherwise indicated.

The composition is provided in liquid form at ambient, or room, temperature, which will generally be between zero and 50° Centigrade. The composition is held at a pressure that maintains it in liquid form within the specified temperature range. The cleaning step is preferably carried out with the composition at ambient temperature.

The organic co-solvent is, in general, a hydrocarbon co-solvent, including but not limited to alkane, alkene, ether, ester and alcohol cosolvents. Typically the co-solvent is an alkane co-solvent, with C₁₀ to C₂₀ linear, branched, and cyclic alkanes, and mixtures thereof (preferably saturated) currently preferred. The organic co-solvent preferably has a

Example 2

3-([2-hydroxy-3-diethylamino]propoxy) propyl terminated polydimethylsiloxane as described above is synthesized as follows. Starting with epoxypropoxypropyl terminated polydimethylsiloxane with an average molecular weight range of 900-1100 g/mole, the siloxane and a 5 molar excess of diethyl amine are added to a round bottom flask equipped with a reflux condenser. A heating bath is applied to the round bottom flask with a bath temperature of about 78° C. and the mixture is refluxed under a static argon head pressure for about 48 hours. The product is isolated by distilling the excess diethyl amine from the polymer and exposing the polymer to a vacuum <1 mm Hg for 12 hours.

The foregoing is illustrative of the present invention, and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

That which is claimed is:

1. A method for cleaning garments or fabrics in carbon dioxide, comprising:

contacting a garment or fabric article to be cleaned with a liquid dry cleaning composition for a time sufficient to clean the article, said liquid dry-cleaning composition comprising a mixture of carbon dioxide, water, and a surfactant

wherein said surfactant is an end-functional polysiloxane surfactant; and wherein said surfactant has the formula X_1-A-X_2 , wherein X_1 and X_2 are end-functional CO_2 -phobic groups, and A is a polysiloxane group; and then

separating the article from the liquid dry cleaning composition.

2. A method according to claim 1, wherein said liquid dry cleaning composition is at a temperature of 0° C. to 30° C.

3. A method according to claim 1, wherein said surfactant is 3-([2-hydroxy-3-diethylamino]propoxy) propyl terminated polydimethylsiloxane.

4. A method according to claim 1, said composition further comprising an organic co-solvent.

* * * * *